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# THE ACCELERATED CORROSION OF METALS

David A. Jackson, Jr.

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Prepared By

Senior Investigator: Henry Leidheiser, Jr.
Associate: David A. Jackson, Jr., Research Chemist

April 21, 1961

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# SECTION I

## The Oxidation of Aluminum in Contact with Mercuric Halides

# INTRODUCTION

Preliminary phases of the quantitative studies of the oxidation of aluminum in contact with mercuric halides, have been reported in the Fifth Quarterly Report. (1) These studies have continued; out of the several systems included in the program, the Al-$HgI_2$ system has been chosen for quantitative measurements of the oxidation rates.

It was found necessary to control the temperature inside the system to a higher degree than in previous determinations. In order to do this, the entire apparatus has been rebuilt and a new, double-walled thoroughly insulated reaction vessel made. A description of this vessel is found in the following sections.

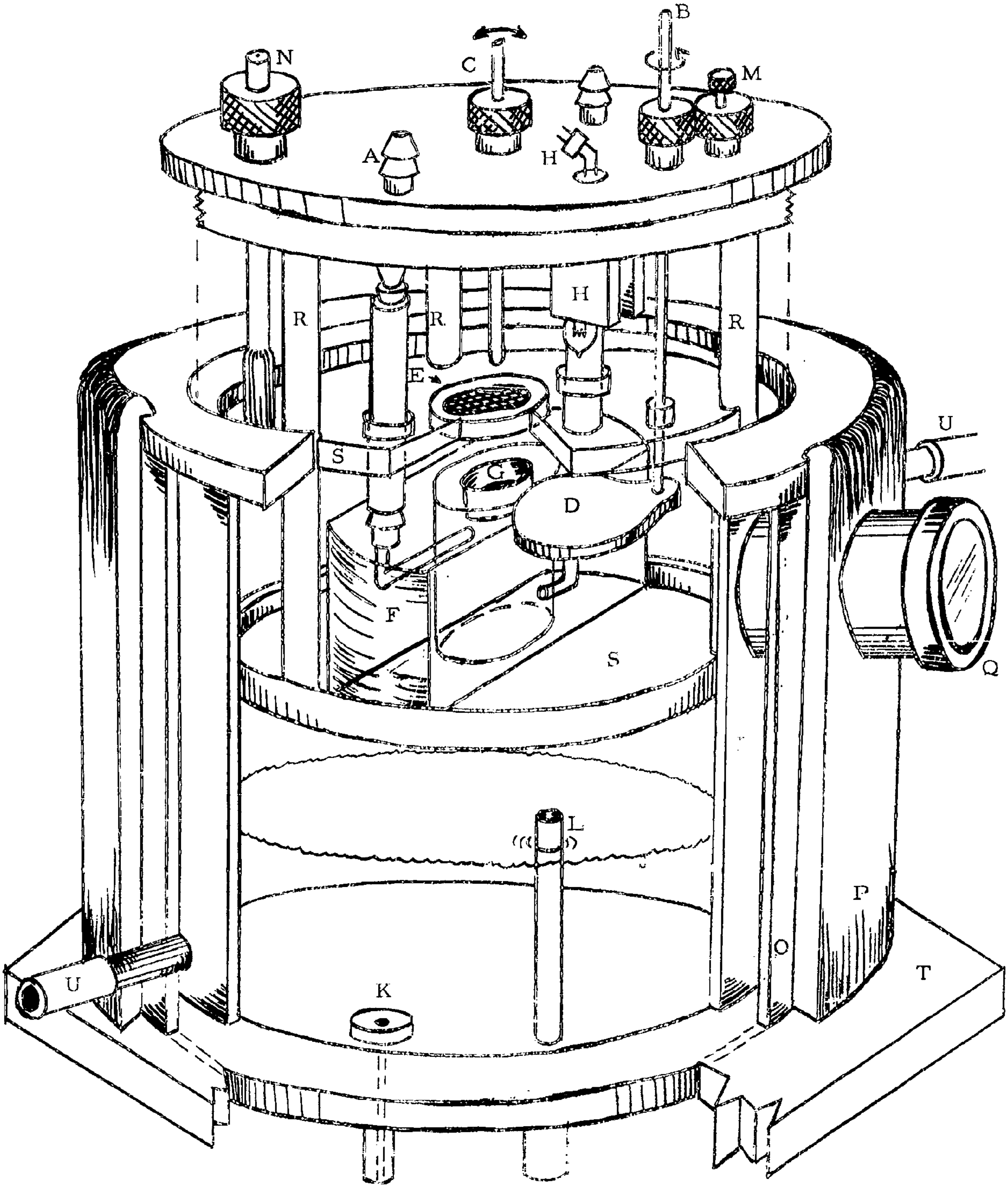
## DESCRIPTION OF APPARATUS

Essentially, the apparatus was identical to that described in the previous report (1), (see page 4 and Fig. 2, page 6). The Plexiglas reaction vessel, however, was replaced by a thoroughly insulated, double-walled, copper reaction chamber. The entire interior metal surface was heavily coated with a black paint to eliminate any corrosive action on the chamber.

A capillary mercury manometer was added for pressure change measurements beyond those of the water manometer. Measurements of the pressure changes in the early stages of the reaction were read with the water manometer, whereas in the later stages, the water manometer was shut-off and the mercury manometer was used. Conversion of the pressure changes in cm $H_2O$ to mm Hg were made before calculations of the weight of oxygen consumed (See Figure 1 for a diagram of this reaction chamber).

Figure 1

(See Page 5 for Description of Apparatus)


B
N
C
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A
H
H
R
R
R
E
U
S
G
D
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L
P
O
T
U
K

| | |
|---|---|
| A. | Water Connections to Sample Jacket |
| B. | Sealed Shield Rod |
| C. | Sealed Agitator Rod |
| D. | Shield |
| E. | Nylon Gauge Sieve |
| F. | Sample Water Jacket |
| G. | Sample Cup |
| H. | Bulb, Housing and Sealed Connection |
| I. | Inner Jacket |
| J. | Water Level |
| K. | Capillary Water Manometer |
| L. | Capillary Mercury Manometer |
| M. | Equilizing Bleeder |
| N. | Sealed Thermometer |
| O. | Outer Jacket |
| P. | Asbestos Insulation |
| Q | Sealed Observation Window |
| R. | Plastic Posts |
| S. | Plastic Tables |
| T. | Base |
| U. | Water Connections to Outer Jacket |

Description of Apparatus in Figure 1, Page 4.

# EXPERIMENTAL PROCEDURE

Reynolds 99.999% Al samples were machined in the shape of 1/2" diameter cylinders, 1/4" thick; degreased in $Et_2O$; etched in 2M HCl solution; washed and dried. Exposed surface areas measured approx. 1.25 $cm^2$. A sample was placed in the cup (G) of the water jacket (F), and the movable shield (D) rotated to a position above the sample. A small amount of salt was placed on the nylon grid (E) and the entire upper section screwed tightly into the reaction chamber.

Connections to the constant temperature bath were made at (A) and (U) and the circulating pump turned on. After thermal equilibrium had been established, both manometers were read, temperature and barometric pressure noted, and the shield (D) rotated to one side of the sample. Agitation of the nylon grid with the stainless steel rod deposited a uniform thickness of $HgI_2$ on the aluminum sample below. The time was noted for the initial readings. Measurements of time, temperature and pressure changes were made at 5 to 10 minute intervals until the oxidation slowed or completely stopped.

Usually the barometric pressure remained essentially constant throughout the individual experiment. When changes in barometric pressure occured over a long length of time, these were noted, and corrections in the pressure readings were made.

Values of $\Delta P$, when in cm $H_2O$, were converted to mm Hg. Certain values of $\Delta P$ in mm Hg were then converted to the corresponding weights of oxygen consumed at the various times. The conversion of $\Delta P$ in mm Hg to $\Delta W_{O_2}$ in mg/cm$^2$ was made from the following equation:

$$\Delta W_{O_2} = 1.356 \left[0.376\, P_t - \frac{{}^{*}44.8}{P_t} - 10.57 \cdot \Delta P\right] \left[\frac{\Delta P}{(P_t - \Delta P)}\right]$$

where $P_t$ and $\Delta P$ were the barometric pressure (total initial pressure) and the pressure changes respectively. This equation applies to the runs at 30° only. Slightly different equations apply at other temperatures. This gives the weight of oxygen consumed by the osidation of aluminum in terms of the initial total pressure and the measured pressure changes.

The numerical values in the equation were derived with consideration of the temperature, vapor pressure of water, and percentage $O_2$ gas in dry air.

Values of $\Delta W$ were plotted vs. time for each experiment. Figures 2 to 5 were experiments run at 30° ± 0.5°C and values of $\Delta W$ were found from the above equation. Figures 6 to 12 were experiments run at temperatures other than 30° and values for $\Delta W$ were found from equations similar to the above. The scales on all graphs are identical .

---

*Note: The term $44.8/P_t$ may be assumed negligible under these conditions.

# RESULTS AND DISCUSSION

The rate curves obtained during the oxidation of aluminum in contact with mercuric iodide were linear during a significant time interval. These linear portions of the curves were sometime preceded by an induction period of low rate. The reasons for these lags are not yet understood. Whereas some reactions continued to run for a long time without slowing, others began to tail-off and slow down soon after the linear rate was reached. Observations indicated that the experiments which initially had a long induction period, tended to run to a greater extent both in time and amount of oxygen consumed.

The slopes of the linear portions of the rate curves were approximately the same in many of the experiments. These slopes are listed in Table A. An average of the slopes of the linear portions of all oxidation rate curves gave a value of $1.36 \times 10^{-1}$ mg. $O_2/cm^2$/minute.

Further study with experiments at temperatures farther from 30°C will be made to determine the importance of temperature on the rate. In Figure 11, the influence of temperature fluctuation may be noted (dotted line) as seen in the values of $\Delta$W. The total temperature variation was 2.15°C.

In Figure 12, readings were not made in the first 130 minutes. Within this time, it was possible that the linear rate of oxidation had already taken place, and the points on the graph only represent the tailing-off period. The approximate slope for this curve was $3.4 \times 10^{-2}$ mg $O_2/cm^2$/min.

# TABLE A

| Slopes of Oxidation Rate Curves $(mg/cm^2/min) \times 10$ | Temperature °C |
|---|---|
| 1.5 | 30.07 |
| 1.3 | 29.97 |
| 1.6 | 30.20 |
| 1.0 | 30.51 |
| 1.2 | 25.2 |
| 1.3 | 25.5 |
| 1.2 | 26.0 |
| 1.3 | 26.9 |
| 1.7 | 28.0 |

Figure 2

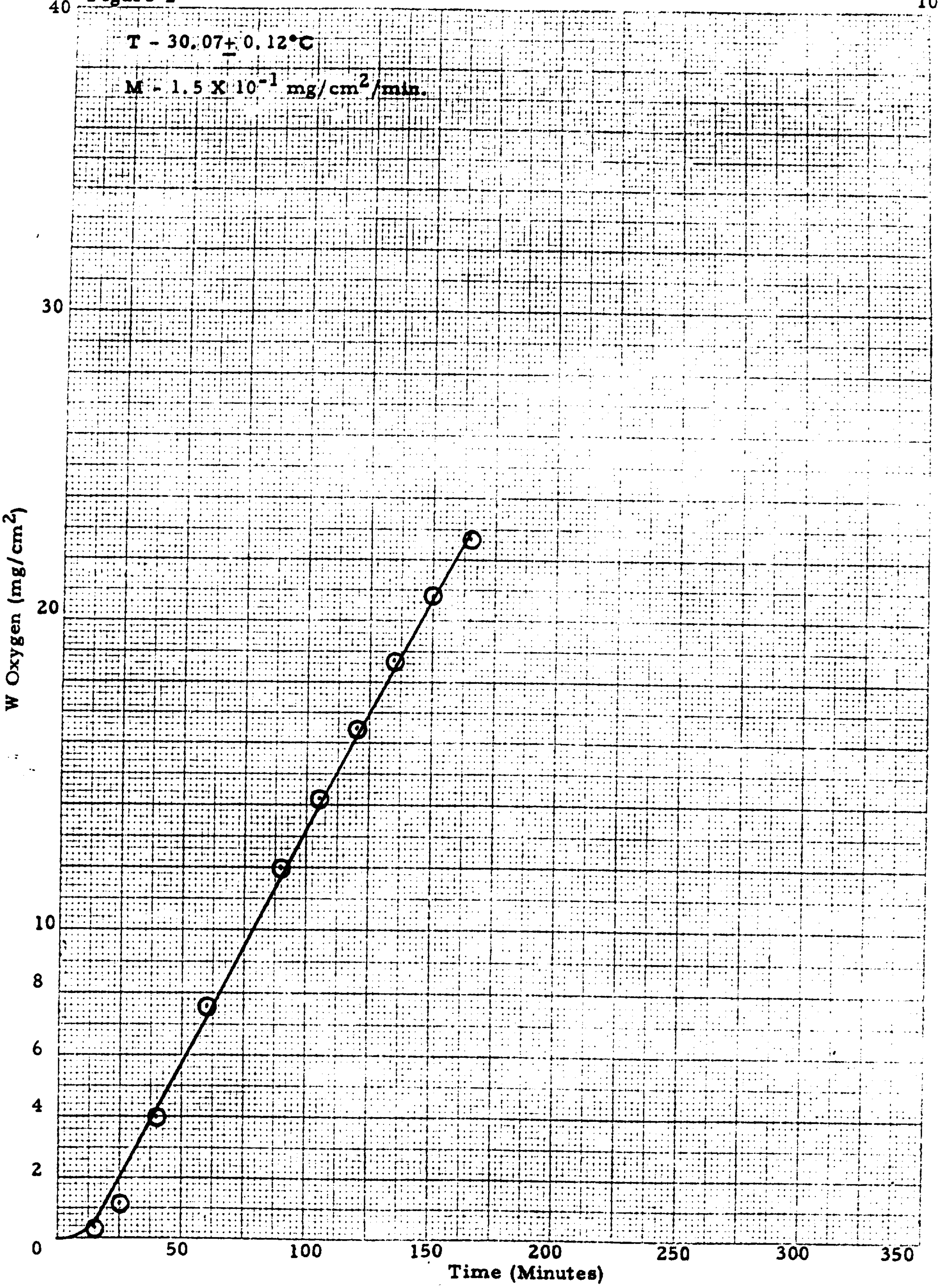

T - 30.07 ± 0.12°C
M - 1.5 X $10^{-1}$ mg/cm$^2$/min.
W Oxygen (mg/cm$^2$)
40
30
20
10
8
6
4
2
0
50
100
150
200
250
300
350
Time (Minutes)

Figure 3

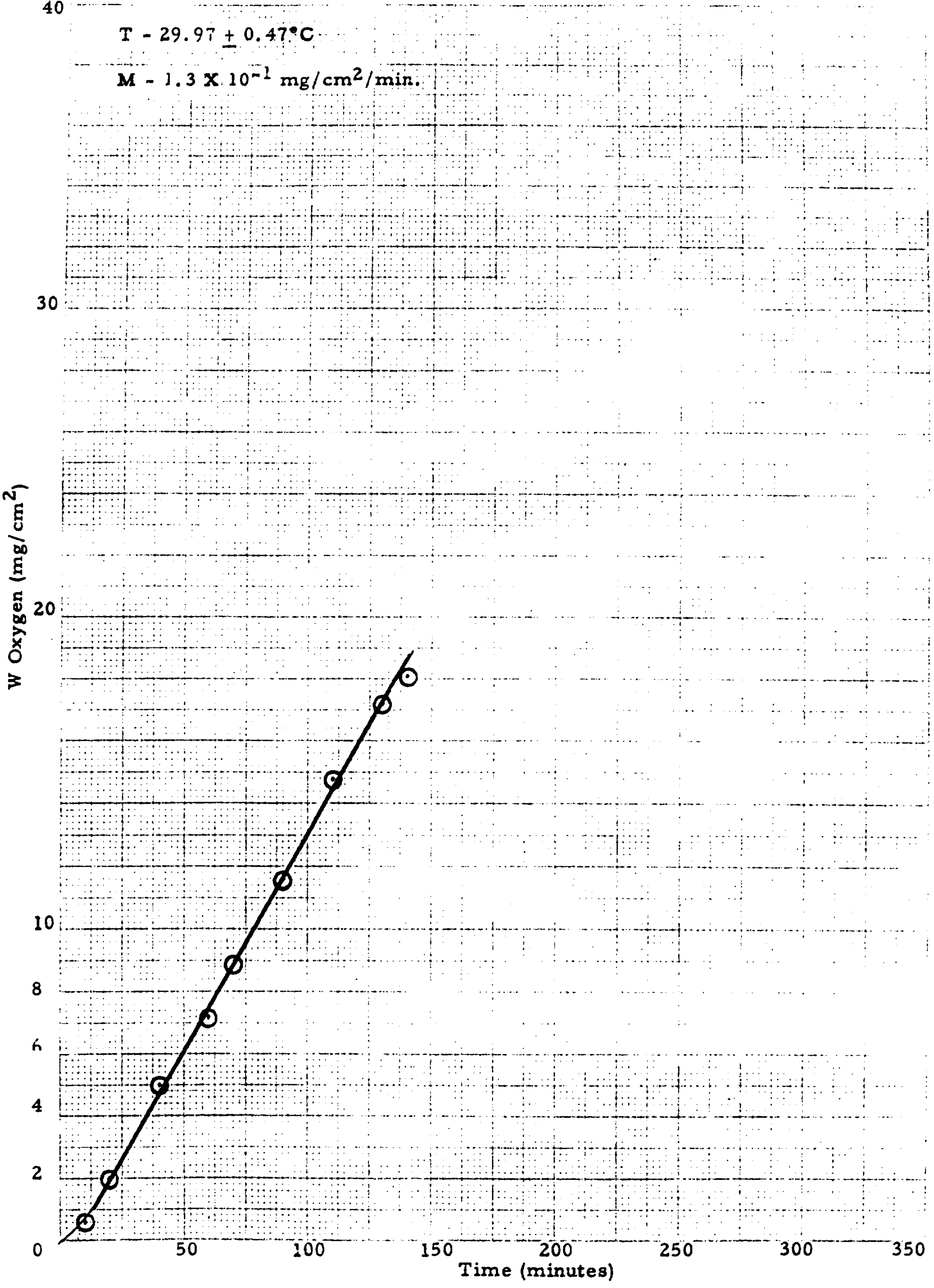
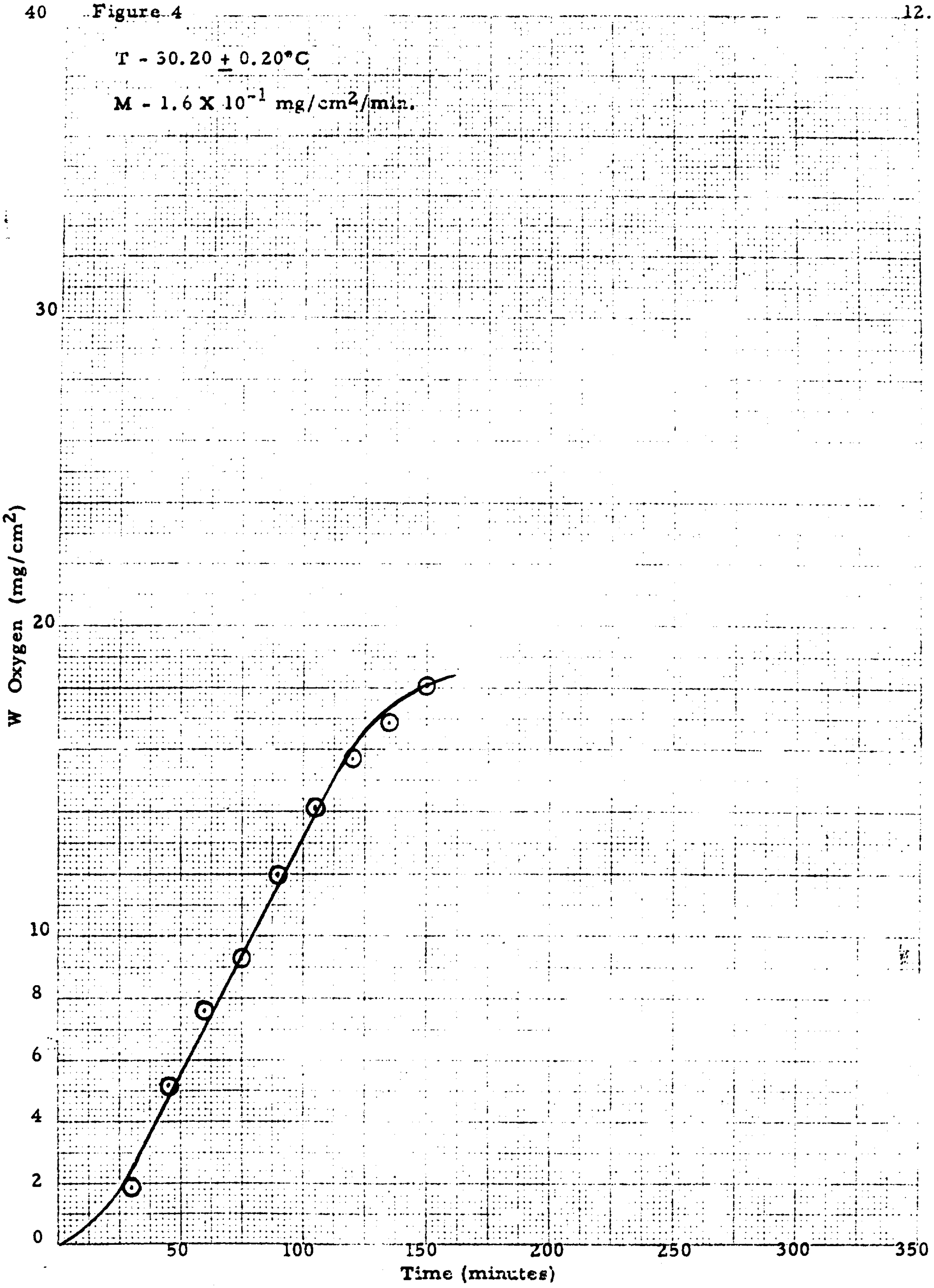

T - 29.97 ± 0.47°C
M - 1.3 X $10^{-1}$ mg/cm$^2$/min.
W Oxygen (mg/cm$^2$)
40
30
20
10
8
6
4
2
0
50
100
150
200
250
300
350
Time (minutes)

Figure 4


T - 30.20 ± 0.20°C
M - 1.6 X 10$^{-1}$ mg/cm$^2$/min.
W Oxygen (mg/cm$^2$)
40
30
20
10
8
6
4
2
0
50
100
150
200
250
300
350
Time (minutes)

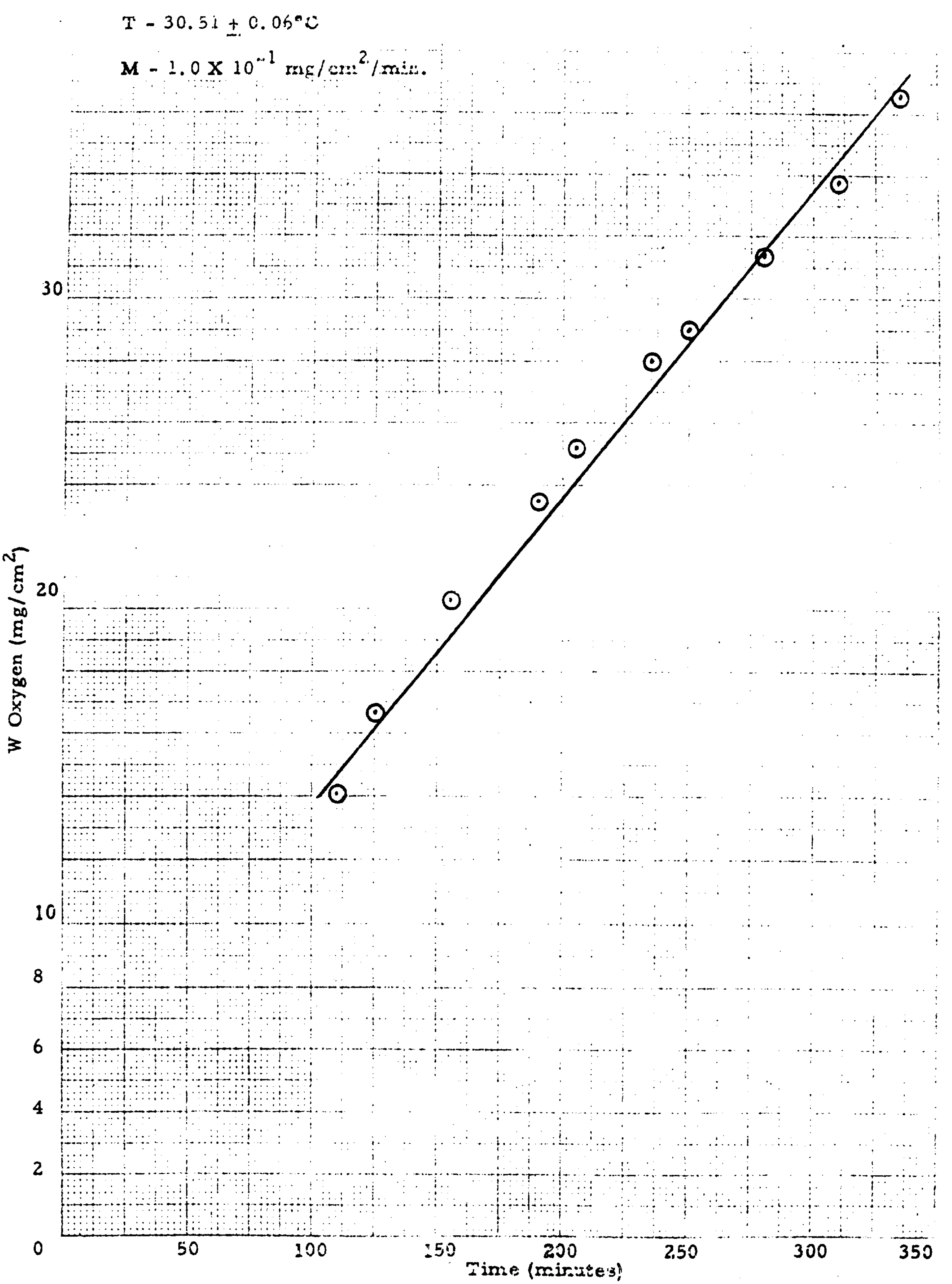


Figure 5

T - 30.51 ± 0.06°C

M - $1.0 \times 10^{-1}$ mg/cm$^2$/min.

Figure 6

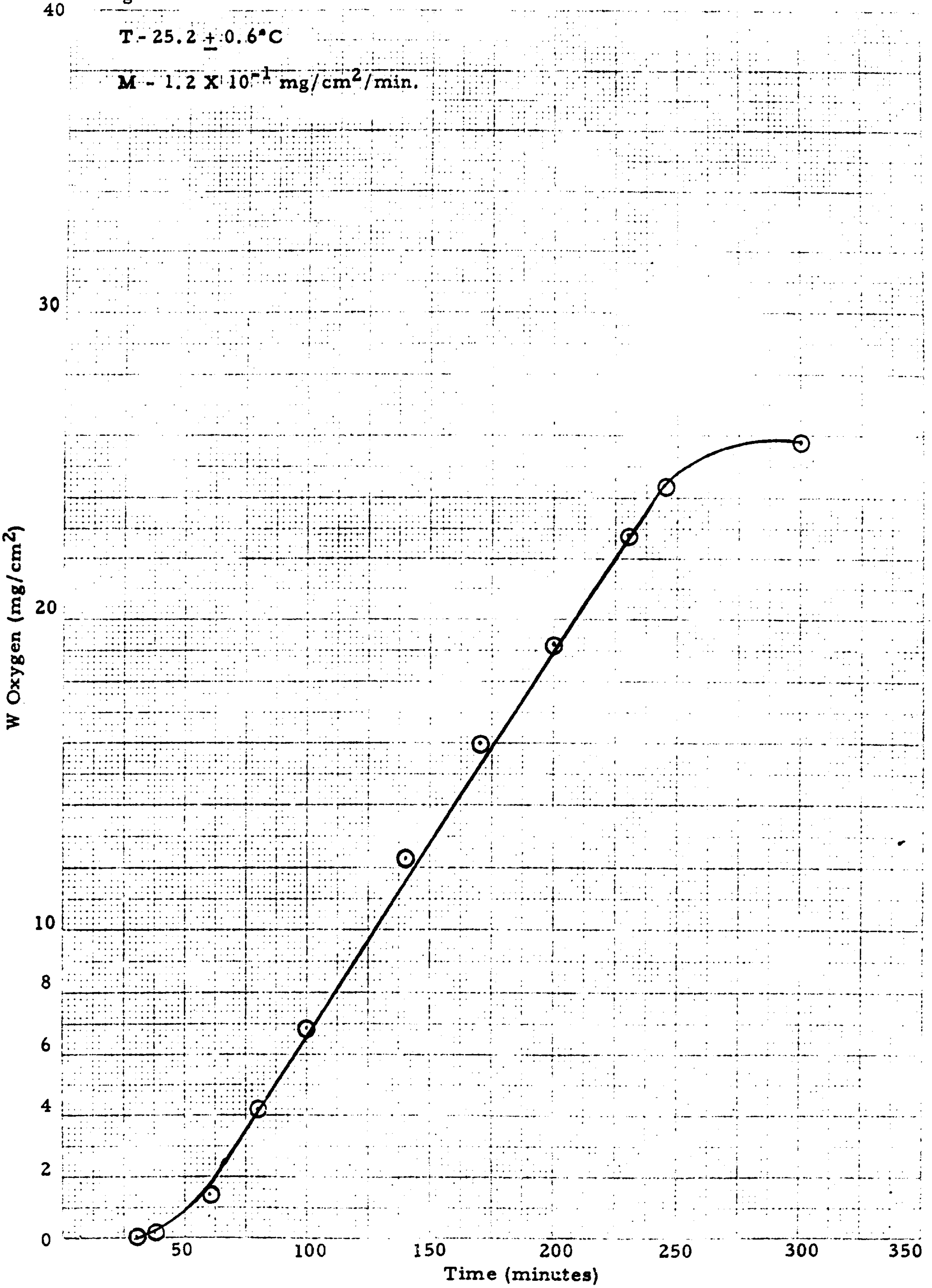

T - 25.2 ± 0.6°C
M - 1.2 X 10^-1 mg/cm^2/min.
W Oxygen (mg/cm^2)
40
30
20
10
8
6
4
2
0
50
100
150
200
250
300
350
Time (minutes)

Figure 7

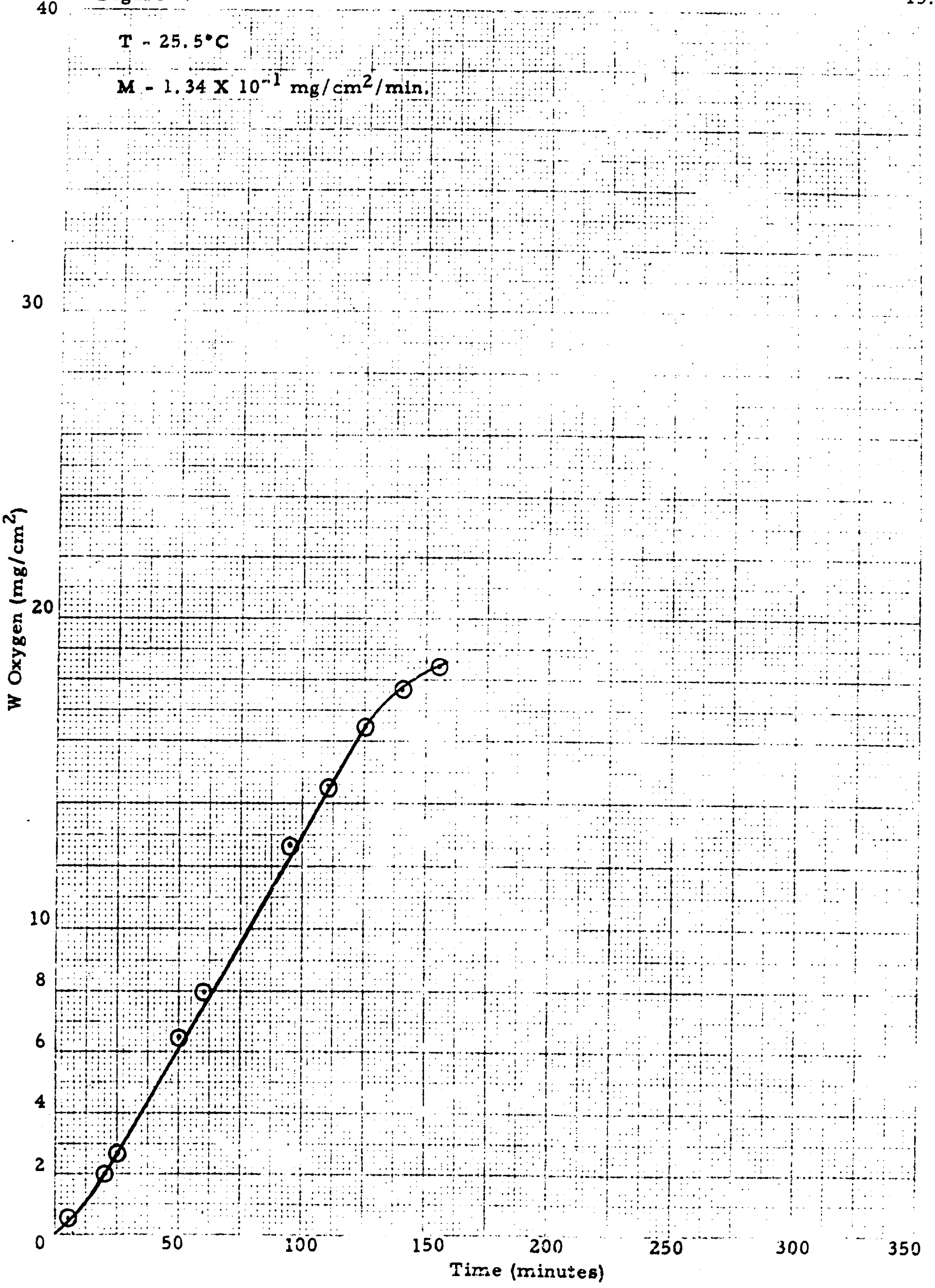

T - 25.5°C
M - 1.34 X $10^{-1}$ mg/cm$^2$/min.
W Oxygen (mg/cm$^2$)
40
30
20
10
8
6
4
2
0
50
100
150
200
250
300
350
Time (minutes)

Figure 8

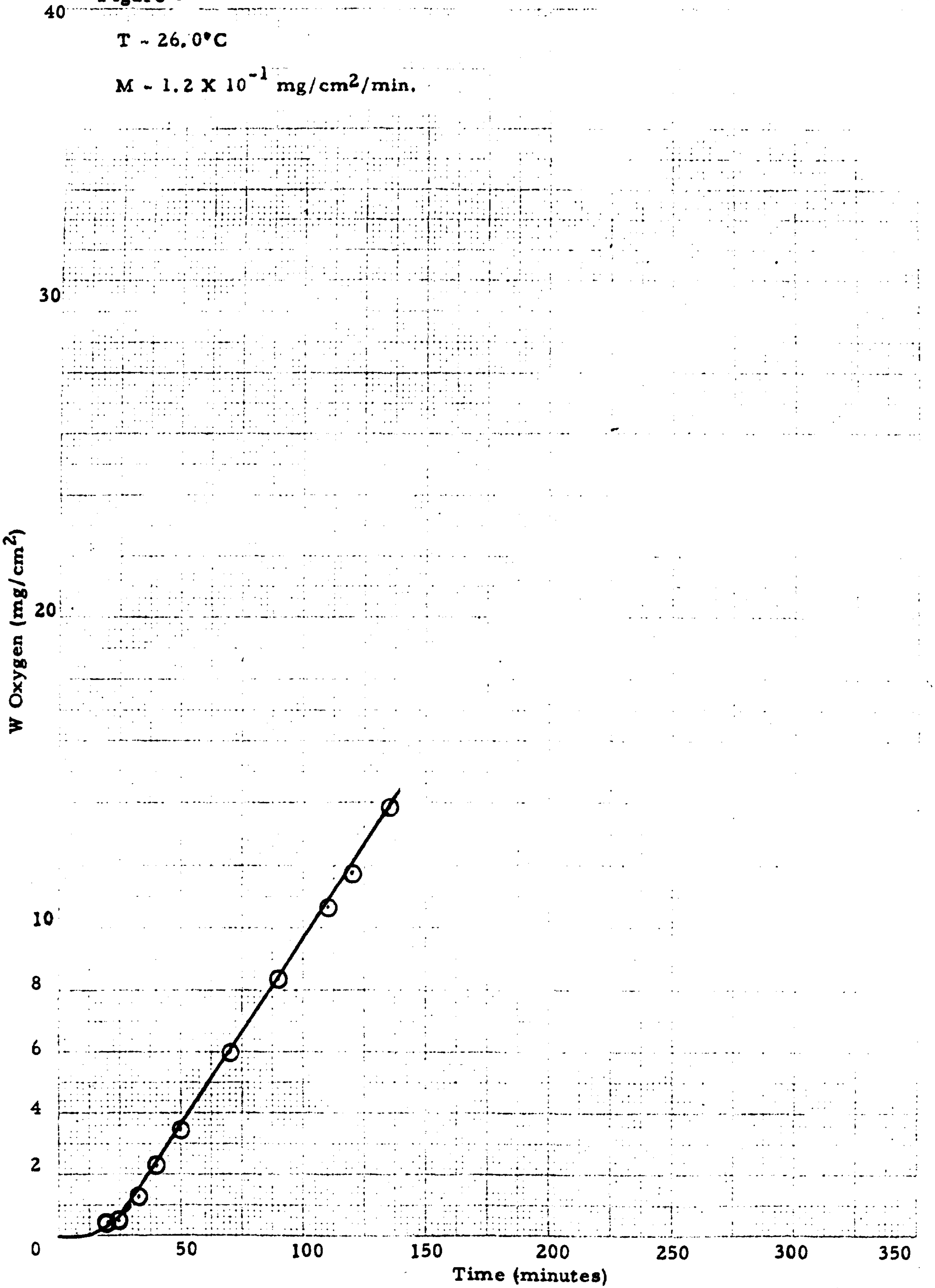

T ~ 26.0°C
M ~ 1.2 X $10^{-1}$ mg/cm²/min.
W Oxygen (mg/cm²)
40
30
20
10
8
6
4
2
0
50
100
150
200
250
300
350
Time (minutes)

Figure 9

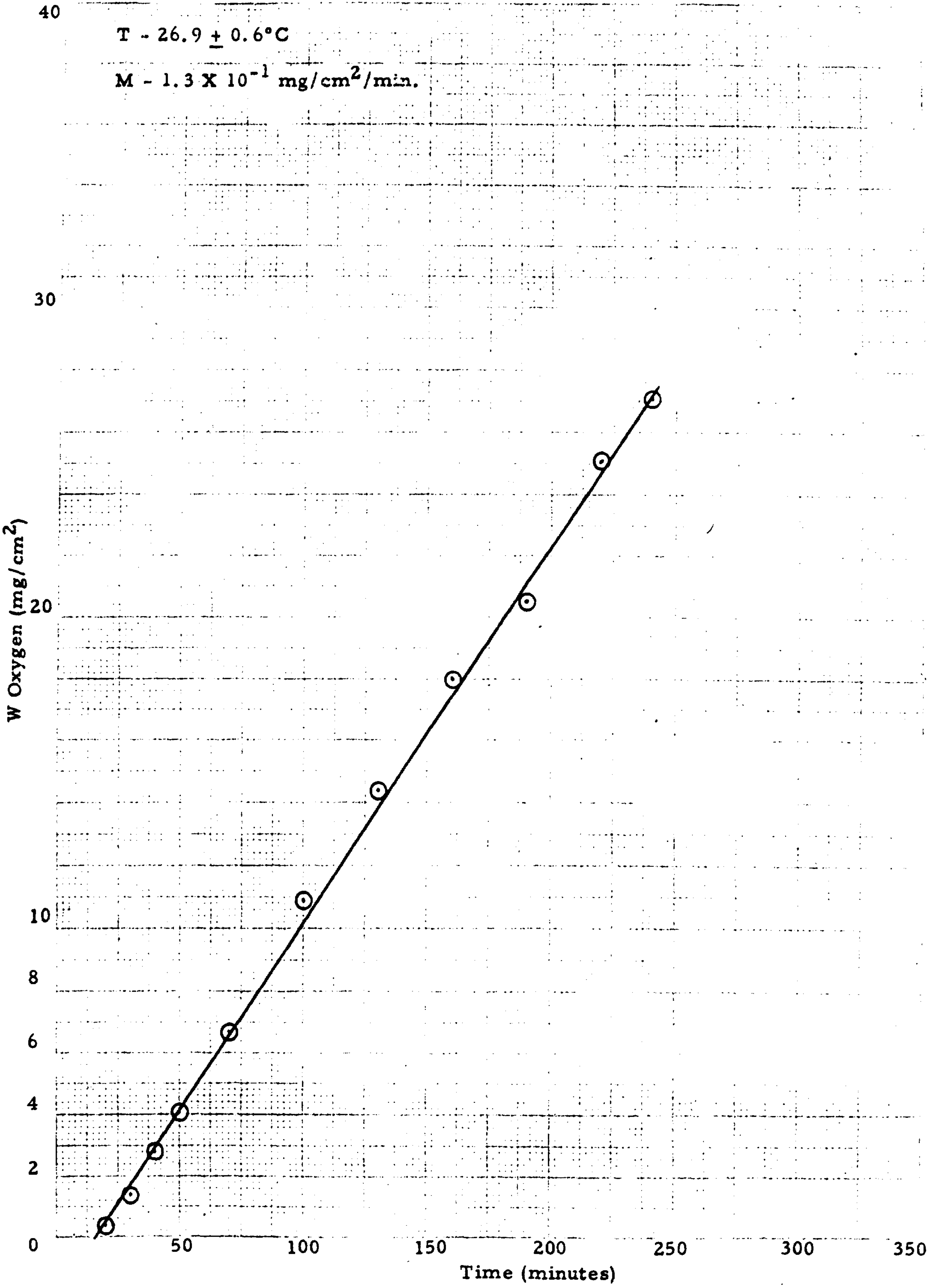

T - 26.9 ± 0.6°C
M - 1.3 X 10$^{-1}$ mg/cm$^2$/min.
40
30
20
10
8
6
4
2
0
W Oxygen (mg/cm$^2$)
50
100
150
200
250
300
350
Time (minutes)

Figure 10.

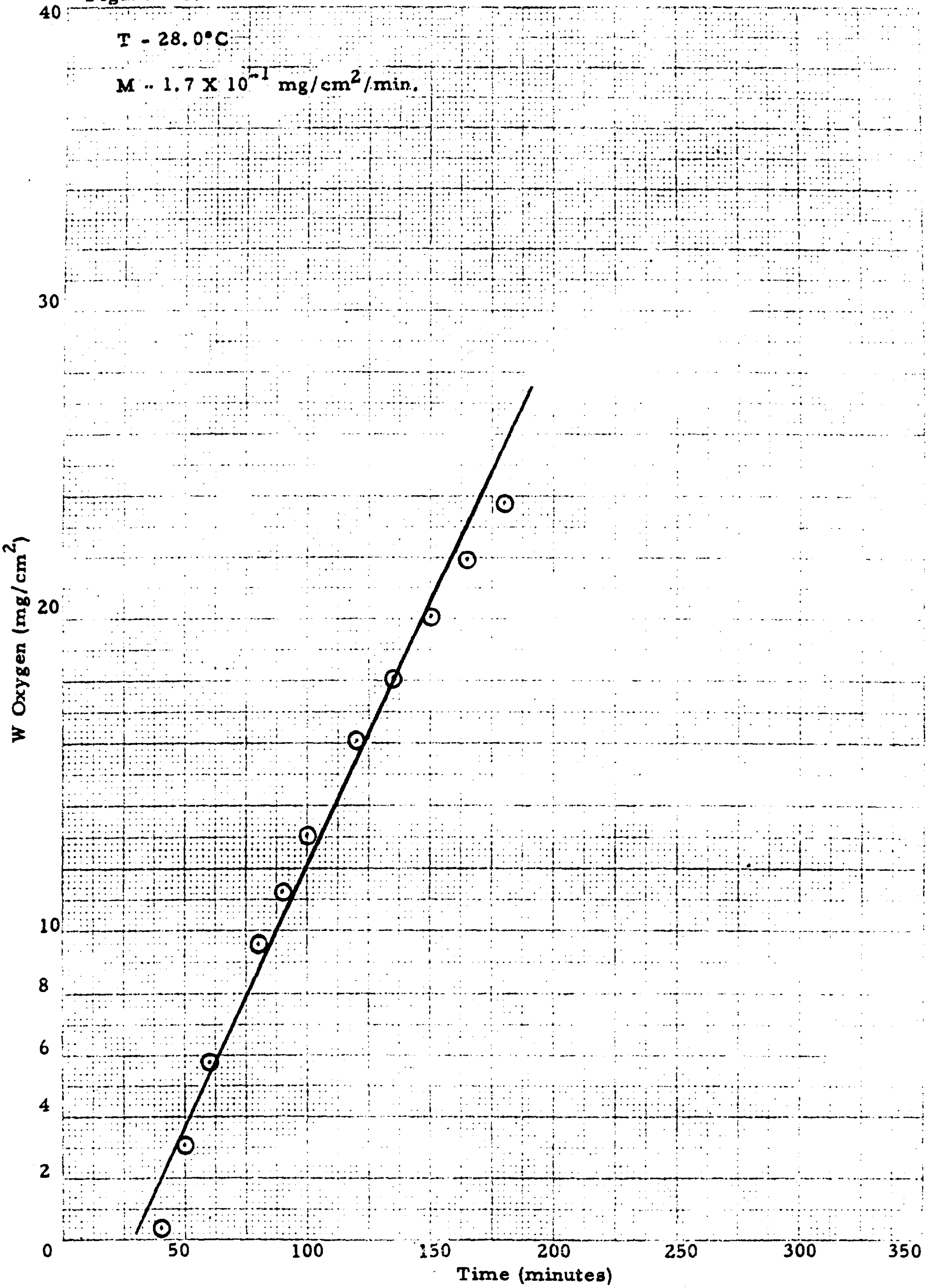
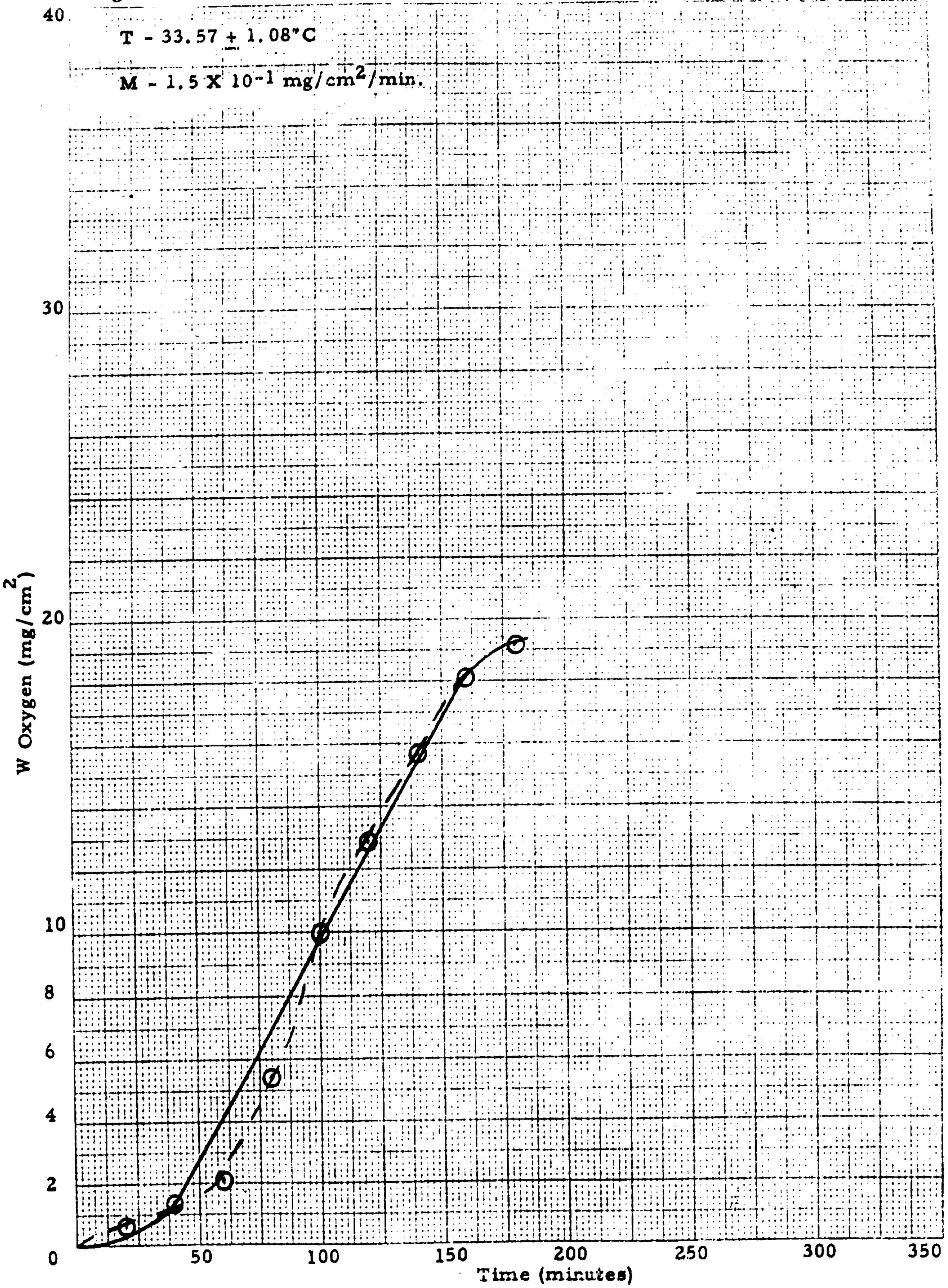

T - 28.0°C
M ~ 1.7 X 10$^{-1}$ mg/cm$^2$/min.
40
30
20
10
8
6
4
2
0
W Oxygen (mg/cm$^2$)
0
50
100
150
200
250
300
350
Time (minutes)

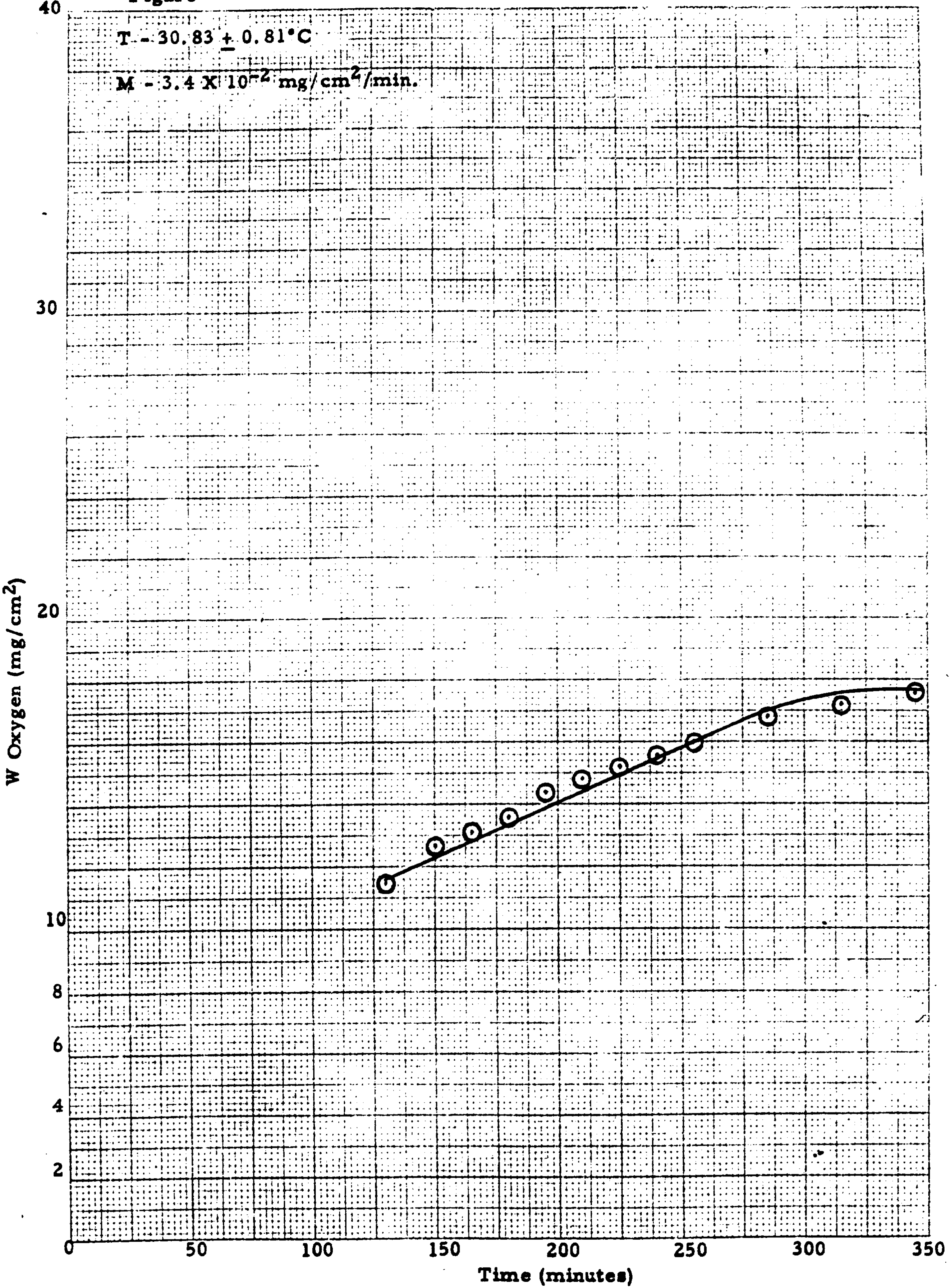
Figure 11



T - 33.57 ± 1.08°C

M - 1.5 X $10^{-1}$ mg/$cm^2$/min.

Figure 12


T - 30.83 ± 0.81°C
M - 3.4 X $10^{-2}$ mg/cm$^2$/min.
40
30
20
10
8
6
4
2
0
50
100
150
200
250
300
350
W Oxygen (mg/cm$^2$)
Time (minutes)

# SECTION II

## The Corrosion of Copper in Mineral Acids in the Presence of Group VIII Chlorides

# INTRODUCTION

In the previous report (1) a survey was made of the effect of platinum metal chlorides on the corrosion of iron in mineral acids at room temperature. It was observed that: (a) platinum was the most effective in accelerating the corrosion of iron in both HCl and $H_2SO_4$; (b) in some cases rates of corrosion were 1000 times that of the blank; (c) in some cases the combined action of two group VIII chlorides was greater than the sum of their individual activities.

In the present report a brief survey has been made of the effect of group VIII chlorides on the corrosion of copper in HCl, $H_2SO_4$, and $HNO_3$. No instances of accelerated corrosion were observed in these systems. Palladium was an excellent inhibitor for the corrosion of copper in 2M $HNO_3$, however.

# EXPERIMENTAL PROCEDURE

Copper, 99.999% pure, was obtained from the American Smelting and Refining Company in the form of rods, 3/8" in diameter. Corrosion samples, 1/4" in length, were machined from the rods. These samples were cleaned in ether and then etched in 2M $HNO_3$ just prior to use.

The corrosion experiments were carried out at room temperature in 250 ml. Erlenmeyer flasks using 100 ml. of acid. No agitation was used. The extent of corrosion was determined gravimetrically.

## RESULTS

Corrosion in 1M $H_2SO_4$ in the Presence of $10^{-4}$M Group VIII Chloride. The results of these experiments are summarized in Table I. In all cases the rate of corrosion was slightly greater than that of the blank, but in no case was there a large rate of corrosion. Probably the increased rate over the blank is a result of the dissolution of a small amount of copper by a metal replacement reaction.

Corrosion in 1M $H_2SO_4$ in the Presence of $10^{-3}$M Group VIII Chloride. The results of these experiments are summarized in Table II. In no case was a large rate of corrosion observed. In all cases the presence of the group VIII chloride in the acid caused a slight increase in the rate of corrosion.

Corrosion in 2M HCl in the Presence of $10^{-3}$M Group VIII Chloride. The results of these experiments are summarized in Table III. In no case was a large rate of corrosion observed. In all cases the presence of the group VIII chloride in the acid caused a slight increase in the rate of corrosion.

Corrosion in 2M $HNO_3$ in the Presence of $10^{-4}$M Group VIII Chloride. The results of these experiments are summarized in Table IV. The copper corroded, as is well known, at an appreciable rate in the 2M $HNO_3$ in the absence of any additive. In all cases the presence of the group VIII chloride reduced the rate, with the effective degree of inhibition decreasing in the order: Pd, Pt, Rh, Ru, Co, Ir, Os, Ni.

With the exception of the experiments with additions of palladium or platinum, the corrosion rate increased with time. This phenomenon is well known and has been attributed (2) to the catalytic effect of the nitrogen oxides which are a product of the reaction.

Corrosion in 2M $HNO_3$ in the Presence of $10^{-3}$M Group VIII Chloride. The results of these experiments are summarized in Table V. Palladium, platinum, rhodium, cobalt, and nickel additions were effective in decreasing the rate of corrosion. Iridium, ruthenium, and osmium additions reduced the corrosion rate slightly but to no major extent. No cases were found in which the corrosion rate was increased.

TABLE I

The Corrosion of Copper in 1M $H_2SO_4$ at Room Temperature in the Presence of $10^{-4}$M Group VIII Chlorides

| Group VIII Chloride | Average Corrosion Rate over a 24-Hour Period ($mg/cm^2/hr$) |
|---|---|
| Co | 0.014 |
| Ni | 0.017 |
| Ru | 0.014 |
| Rh | 0.022 |
| Pd | 0.018 |
| Os | 0.019 |
| Ir | 0.017 |
| Pt | 0.021 |
| Blank | 0.007 |

## TABLE II

The Corrosion of Copper in 1M $H_2SO_4$ at Room Temperature in the Presence of $10^{-3}$M Group VIII Chlorides

| Group VIII Chloride | Average Corrosion Rate over a 24-Hour Period (mg/cm$^2$/hr) |
|---|---|
| Co | 0.010 |
| Ni | 0.017 |
| Ru | 0.016 |
| Rh | 0.014 |
| Pd | 0.045 |
| Os | 0.017 |
| Ir | 0.013 |
| Pt | 0.035 |
| Blank | 0.006 |

## TABLE III

The Corrosion of Copper in 2M HCl at Room Temperature in the Presence of $10^{-3}$M Group VIII Chlorides

| Group VIII Chloride | Average Corrosion Rate over a 24-Hour Period (mg/cm$^2$/hr) |
|---|---|
| Co | 0.029 |
| Ni | 0.026 |
| Ru | 0.052 |
| Rh | 0.056 |
| Pd | 0.034 |
| Os | 0.043 |
| Ir | 0.029 |
| Pt | 0.077 |
| Blank | 0.021 |

## TABLE IV

The Corrosion of Copper in 2M $HNO_3$ at Room Temperature in the Presence of $10^{-4}$M Group VIII Chlorides

| Group VIII Chloride | Corrosion in mg/cm$^2$ | | |
|---|---|---|---|
| | 1 Hr. | 3 Hrs. | 24 Hrs. |
| Co | 1.1 | 5.0 | 149 |
| Ni | 1.0 | 5.9 | 246 |
| Ru | 2.0 | 2.8 | 130 |
| Rh | 0.2 | 1.3 | 45 |
| Pd | 0.1 | 0.4 | 0.8 |
| Os | 0.7 | 5.0 | 238 |
| Ir | 0.8 | 4.7 | 160 |
| Pt | 0.8 | 2.1 | 19 |
| Blank | 1.6 | 9.5 | 247 |

---

## TABLE V

The Corrosion of Copper in 2M $HNO_3$ at Room Temperature in the Presence of $10^{-3}$M Group VIII Chlorides

| Group VIII Chloride | Average Corrosion Rate over a 24-Hour Period (mg/cm$^2$/hr) |
|---|---|
| Co | 0.014 |
| Ni | 0.014 |
| Ru | 6.4 |
| Rh | 0.062 |
| Pd | 0.044 |
| Os | 8.0 |
| Ir | 2.6 |
| Pt | 0.081 |
| Blank | 9.3 |

## DISCUSSION

In these preliminary studies with mineral acids no evidence was found for an appreciable increase in the corrosion rate of copper in the presence of dissolved group VIII transition metal chlorides. This result is to be expected since the group VIII metals are effective in accelerating the corrosion rates of less noble metals by virtue of their ability to catalyze the cathodic hydrogen evolution reaction. In the case of copper, the reaction $Cu + 2HX = Cu^{++}(aq) + H_2(g) + 2X^-(aq)$, is unfavorable from a thermodynamic point of view in the presence of minute amounts of hydrogen gas. On the other hand, reactions involving the scavenging of hydrogen by oxidizing agents, in which the product of the overall reaction is not gaseous hydrogen, are favored from a thermodynamic viewpoint. In the absence of hydrogen evolution the platinum metals would not be expected to be effective catalysts for the dissolution reaction.

The most interesting results are those shown in Tables IV and V in which appreciable inhibition of the reaction with $HNO_3$ was observed. Limiting the analysis to the inert platinum metals, it will be noted that the effectiveness of these metals in inhibiting the corrosion in $HNO_3$ may be described as follows:

| | Effectiveness in Inhibiting the Corrosion in 2 M $HNO_3$ at 2 Concentrations of the Pt Metal | |
|---|---|---|
| | $10^{-4}$M | $10^{-3}$M |
| Good Inhibitor | Pd | Pd, Pt, Rh |
| Moderate Inhibitor | Pt, Rh | none |
| Poor Inhibitor | Ru, Ir, Os | Ru, Ir, Os |

At both concentrations, palladium was the most effective inhibitor, followed by platinum and rhodium. Ruthenium, iridium, and osmium were only slightly effective. In previous studies carried out in this laboratory (3) it was hypothesized that good inhibition of the anodic reaction was often obtained in reactions with boiling acids under conditions where the inhibiting metal had an appreciable solubility in the corroding metal. For example, palladium is an excellent inhibitor for the corrosion of silver in constant-boiling HCl and copper is an excellent inhibitor for the corrosion of nickel in boiling 2M HCl. Palladium-silver and copper-nickel form solid solutions over the entire range of concentration. In the systems used in the present study, the phase diagrams of the copper-palladium and copper-platinum systems indicate complete solid solution over the entire concentration range. In the copper-rhodium system, the solubility of copper in rhodium is of the order of 20 atomic % at room temperature. On the other hand, ruthenium, iridium, and osmium have little or no solubility in copper (4). It is not desired to pursue this analysis too far at the present time until additional critical experiments can be performed.

# BIBLIOGRAPHY

(1) David A. Jackson, Jr., and Henry Leidheiser, Jr., Fifth Quarterly Report to the Army Chemical Center under Contract No. DA 18-108-405-CML-518, January 19, 1961.

(2) U. R. Evans, "The Corrosion and Oxidation of Metals: Scientific Principles and Practical Applications,: Edward Arnold, Ltd., London, 1960, pp 324-7.

(3) W. Roger Buck, III, and Henry Leidheiser, Jr., unpublished experiments

(4) M. Hansen, "Constitution of Binary Alloys," McGraw-Hill Book Co., New York, 1958.